Quasi-exact evaluation of the magnetic properties of a giant Keplerate molecule

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Abstract –In this Letter we report how thermodynamic properties of a giant frustrated magnetic Keplerate molecule of $N = 30$ spins $s = 1/2$ can be evaluated with the help of the highly accurate finite-temperature Lanczos method. The comparison to experimental data shows excellent agreement. Since this molecule is structurally related to the archetypical kagomé lattice antiferromagnet we expect new detailed insight into properties of this important class of frustrated materials.

Introduction. – Nanometer sized polyoxometalate molecules constitute a fascinating class of molecular materials [1–7]. The series of Keplerate molecules $\{Mo_{72}Fe_{30}\}$, $\{Mo_{72}Cr_{30}\}$, $\{Mo_{72}V_{30}\}$, $\{W_{72}V_{30}\}$ is from a magnetism point of view of special interest since in these bodies paramagnetic ions occupy the vertices of a nearly perfect icosidodecahedron – one of the Archemidean solids. These bodies resemble some of the most interesting magnetically frustrated spin lattices such as the kagomé lattice antiferromagnet [8]. Valuable insight about the physics of such lattices can be gained by studying the finite-size bodies. But although icosidodecahedra consist of only $N = 30$ spin sites, the dimension of the Hilbert space for $s = 1/2$ reaches a stunning 1,073,741,824.

Figure 1 shows the structure of the icosidodecahedron: spin sites are displayed by bullets, edges are given as straight lines – in the later used Heisenberg model they represent the interaction pathways. If such interactions are of antiferromagnetic nature, i.e. favour antiparallel alignment in the ground state, a magnetic structure that consists of triangles is said to be frustrated [9]. In this respect the icosidodecahedron belongs to the archetypical class of frustrated spin systems made of corner-sharing triangles as does the two-dimensional kagomé lattice antiferromagnet [8, 10–14]. Compared to other antiferromagnetically coupled spin systems, such as spin rings for instance, these structures possess unusual features generated by the frustration: (1) many low-lying singlet states below the first triplet excitation, (2) an extended plateau of the magnetization at one third of the saturation magnetization when plotted versus field at low temperatures, and (3) a large magnetization jump to saturation again as funtion of applied magnetic field. The last feature is intimately connected with a huge magnetocaloric effect [15, 16].

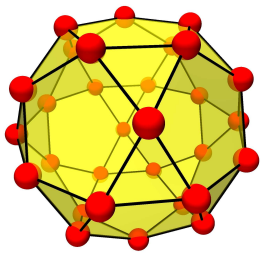

Fig. 1: The core structure of a Keplerate molecule is an icosidodecahedron. The bullets represent the 30 spin sites, the edges indicate the 60 exchange interactions.

For theoretical investigations the extended lattice systems such as the kagomé excape even a numerical treatment since the dimension of the related Hilbert space grows exponentially like $(2s + 1)^N$, where s denotes the spin quantum number of individual spins and N the number of spins treated in the model. Therefore, the existance of finite, i.e. molecular realizations of such frustrated structures provides an opportunity to theoretically investigate the quantum energy spectrum and to understand the related features. A major insight could already

be achieved through the study of icosidodecahedra a couple of years ago. It turned out that the high-field behavior is dominated by special quasi particles, so-called independent magnons [13,17,18].

Nevertheless, the full thermodynamics, i.e. physical observables as function of both temperature and applied field, was so far not available for systems as large as Keplerates. In this Letter we demonstrate for the first time that by means of the finite-temperature Lanczos method (FTLM) [19] the thermodynamic properties of the icosidodecahedron with 30 spins $s = 1/2$ can indeed be evaluated. In an investigation prior to these calculations we demonstrated that the FTLM is a very accurate approximation scheme that provides quasi-exact results [20]. None of the alternative approximations – Density Matrix Renormalization Group techniques (DMRG) [21, 22] or Quantum Monte-Carlo (QMC) [23–25] – is able to deliver these results for such a molecule.

Evaluation of magnetic observables. – Our numerical calculations in the Heisenberg model had to be performed on a supercomputer. We employed the SGI Altix 4700 at the German Leibniz Supercomputing Center using openMP parallelization with up to 510 cores. The complete calculation needed approximately a full week of cpu time on 510 cores. The resulting magnetic observables are shown in Figures 2, 3, and 4. In case of the magnetic susceptibility χ we compare to experimental data that are published for the highly symmetric molecule $\{W_{72}V_{30}\}$ [26].

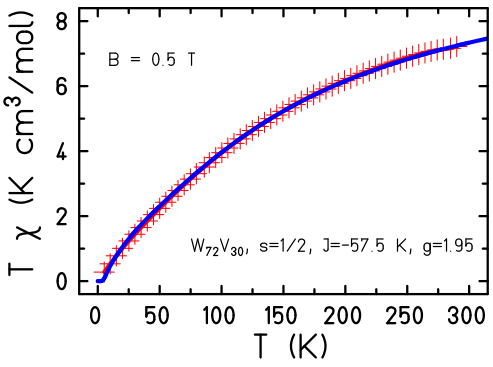

Fig. 2: Susceptibility as function of temperature: Crosses mark the experimental data that are published in [26]. The curve is the result of our simulation.

Figure 2 displays the magnetic susceptibility as a function of temperature for an applied field of $B = 0.5$ T. The low-temperature part demonstrates that the antiferromagnetically coupled ($s = 1/2$) icosidodecahedron is a gapped spin system, i.e. it possesses an energy gap between the singlet ground state and the first excited triplet state. QMC calculations cannot resolve the low-temperature behavior due to the negative-sign problem for frustrated systems. Nevertheless, QMC can accurately determine the high-temperature behavior as is demonstrated in [26]. From this calculation the values of the exchange interaction J as well as of the spectroscopic splitting factor g were adopted.

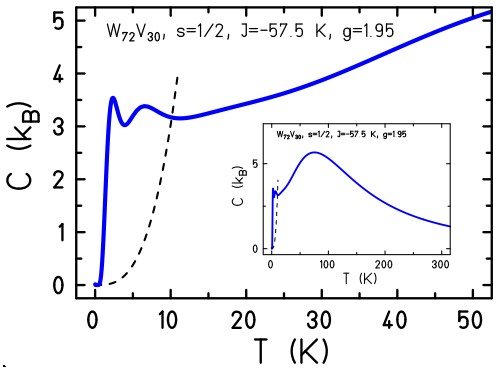

Fig. 3: Heat capacity: the solid curve predicts the behavior of $\{W_{72}V_{30}\}$. The dashed curve provides an estimate for the phonon contribution.

The singlet-triplet gap seen in the susceptibility does not exclude further singlet states below the triplet. Indeed, this is one of the expected frustration hallmarks for the icosidodecahedron [27]. In Figure 3 we predict that for $\{W_{72}V_{30}\}$ these singlets contribute dominantly to the heat capacity below 10 K. The solid curve, that displays the specific heat function at zero field, exhibits pronounced Schottky-like peaks which originate dominantly from the low-lying singlets. The dashed curve provides a reasonable estimate for the additional phonon contribution. In an experiment it should be possible to disentangle the two below 10 K. The inset shows to full curve up to room temperature.

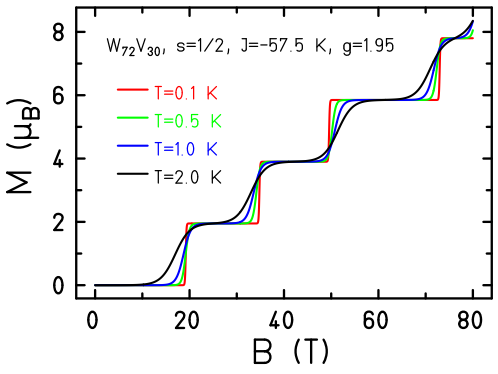

Fig. 4: Magnetization for various temperatures: the steps at low temperatures result from crossings of Zeeman split energy levels.

Figure 4 provides the theoretical estimates for the magnetization curves at various temperatures. Again the singlet-triplet gap is visible, this time as flat $M = 0$ behavior up to the first magnetization step which happens at the level crossing of the lowest $(S = 0, M = 0)$ and $(S = 1, M = -1)$ Zeman levels. In realistic static and pulsed magnetic fields the first three steps of the magnetization curve could be observed.

Summerizing, by means of the finite-temperature Lanczos method (FTLM) we are able to accurately evaluate all thermal properties of a giant magnetic molecule that is structurely related to the kagomé lattice. We hope that these achivements will promote further investigations in the field of quantum magnetism.

Technical details. – The magnetic properties of the Keplerate molecule $\{W_{72}V_{30}\}$ are described by the following model

$$\underset{\sim}{H} = -2J \sum_{<i,j>} \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\,\mu_B\,B \sum_i \underset{\sim}{s}_i^z \ . \quad (1)$$

The first term (Heisenberg Hamiltonian) models the isotropic exchange interaction between spins centered at nearest neighbor sites i and j. $J = -57.5$ K is the antiferromagnetic exchange parameter [26]. The second term (Zeeman term) represents the interaction with the external magnetic field. The spectroscopic splitting factor is taken to be $g = 1.95$ [26].

In the finite-temperature Lanczos method [19] the exact partition function

$$Z(T,B) = \sum_\Gamma \sum_\nu \langle\, \nu,\Gamma \,|\, e^{-\beta \underset{\sim}{H}} \,|\, \nu,\Gamma \,\rangle \quad (2)$$

is approximated by

$$Z(T,B) \approx \sum_\Gamma \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \times e^{-\beta \epsilon_n^{(\nu,\Gamma)}} |\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma \,\rangle|^2 \ . \quad (3)$$

For the evaluation of the right hand side of Eq. (3) $|\,\nu,\Gamma\,\rangle$ is taken as the initial vector of a Lanczos iteration. This iteration consists of N_L Lanczos steps, which span a respective Krylow space. The Hamiltonian is diagonalized in this Krylow space which yields the N_L Lanczos eigenvectors $|\,n(\nu,\Gamma)\,\rangle$ as well as the associated Lanczos energy eigenvalues $\epsilon_n^{(\nu,\Gamma)}$. The number of Lanczos steps N_L is a parameter of the approximation. $N_L \approx 100$ yields good results [20]. R_Γ is the number of random vectors that are considered in the sum instead of the full basis set. Γ labels the irreducible representations of the employed symmetry group. The full Hilbert space is decomposed into mutually orthogonal subspaces $\mathcal{H}(\Gamma)$. An observable would then be calculated as

$$O(T,B) \approx \frac{1}{Z(T,B)} \sum_\Gamma \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(\nu,\Gamma)}} \times \langle\, n(\nu,\Gamma) \,|\, \underset{\sim}{O} \,|\, \nu,\Gamma \,\rangle \langle\, \nu,\Gamma \,|\, n(\nu,\Gamma) \,\rangle \ . \quad (4)$$

For the present calculations we employed the collective rotations of the spin about the z-axis as the symmetry. The resulting subspaces $\mathcal{H}(M)$ for the total magnetic quantum numbers $M = 15, 14, \ldots, 0, \ldots, -14, -15$ were included exactly for $|M| > 10$, since these are small enough. For all other subspaces we choose $R = 20$ and $N_L = 100$.

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REFERENCES

[1] Müller A., Peters F., Pope M. and Gatteschi D., *Chem. Rev.* , **98** (1998) 239.
[2] Müller A., Sarkar S., Shah S. Q. N., Bögge H., Schmidtmann M., Sarkar S., Kögerler P., Hauptfleisch B., Trautwein A. and Schünemann V., *Angew. Chem. Int. Ed.* , **38** (1999) 3238.
[3] Müller A., Kögerler P. and Dress A. W. M., *Coord. Chem. Rev.* , **222** (2001) 193.
[4] Müller A., Luban M., Schröder C., Modler R., Kögerler P., Axenovich M., Schnack J., Canfield P. C., Bud'ko S. and Harrison N., *Chem. Phys. Chem.* , **2** (2001) 517.
[5] Müller A., *Science* , **300** (2003) 749.
[6] Kortz U., Müller A., van Slageren J., Schnack J., Dalal N. S. and Dressel M., *Coord. Chem. Rev.* , **253** (2009) 2315.
[7] Kögerler P., Tsukerblat B. and Müller A., *Dalton Trans.* , **39** (2010) 1.
[8] Rousochatzakis I., Läuchli A. M. and Mila F., *Phys. Rev. B* , **77** (2008) 094420.
[9] Schnack J., *Dalton Trans.* , **39** (2010) 4677 .
[10] Sindzingre P., Misguich G., Lhuillier C., Bernu B., Pierce L., Waldtmann C. and Everts H. U., *Phys. Rev. Lett.* , **84** (2000) 2953.
[11] Moessner R., *Can. J. Phys.* , **79** (2001) 1283.
[12] Atwood J. L., *Nat. Mater.* , **1** (2002) 91.
[13] Schmidt H.-J., Richter J. and Moessner R., *J. Phys. A: Math. Gen.* , **39** (2006) 10673.
[14] Moessner R., *J. Phys.: Conf. Ser.* , **145** (2009) 012001.
[15] Zhitomirsky M. E., *Phys. Rev. B* , **67** (2003) 104421.
[16] Schnack J., Schmidt R. and Richter J., *Phys. Rev. B* , **76** (2007) 054413.
[17] Schnack J., Schmidt H.-J., Richter J. and Schulenburg J., *Eur. Phys. J. B* , **24** (2001) 475.
[18] Schulenburg J., Honecker A., Schnack J., Richter J. and Schmidt H.-J., *Phys. Rev. Lett.* , **88** (2002) 167207.
[19] Jaklic J. and Prelovsek P., *Phys. Rev. B* , **49** (1994) 5065.
[20] Schnack J. and Wendland O., *Eur. Phys. J. B* , (2010) accepted; http://arxiv.org/abs/1009.2889.
[21] White S. R., *Phys. Rev. B* , **48** (1993) 10345.
[22] Schollwöck U., *Rev. Mod. Phys.* , **77** (2005) 259.
[23] Sandvik A. W. and Kurkijärvi J., *Phys. Rev. B* , **43** (1991) 5950.
[24] Sandvik A. W., *Phys. Rev. B* , **59** (1999) R14157.
[25] Engelhardt L. and Luban M., *Phys. Rev. B* , **73** (2006) 054430.

[26] Todea A. M., Merca A., Bögge H., Glaser T., Engelhardt L., Prozorov R., Luban M. and Müller A., *Chem. Commun.* , (2009) 3351.
[27] Schmidt R., Schnack J. and Richter J., *J. Magn. Magn. Mater.* , **295** (2005) 164.